Proton Conducting Solid Electrolyte via Ozonolysis of Cationic Ammonium Organoalkoxysilane Surfactant Templated MCM-41

Supporting Information

Synthetic Details

Materials: All solvents were purified by fractional distillation from the appropriate drying agents or dried by filtration through the appropriate drying agents prior to use.

Experimental:

Synthesis of surfactant 8

(E)-5-chloropent-1-enylboronic acid (2)

Catecholborane (5.85 mmol, 0.7 g) was carefully added to neat chloropent-1-yne (4.9 mmol, 0.5 g) under argon. The mixture was then heated to 100^{o}C under vigorous stirring for 3 hours. The mixture was cooled to 70^{o}C and quenched with (10 mL) water. After 2 hours of stirring, the mixture was further cooled to 0^{o}C, and the resulting white precipitate was filtered over a buchner funnel, washed with cold water and recrystallized from hot water to give the desired product **2** in 60% yield.

(E)-5-chloro-1-iodopent-1-ene (3)

To a mixture of (E)-5-chloropent-1-enylboronic acid (4.9 mmol, 0.73g) in ether (5 mL) at 0^{o}C was added aqueous sodium hydroxide (15 mmol, 5 mL, 3N) followed by elemental Iodine (5.85 mmol, 1.49g in 15 mL ether). The mixture was stirred at 0^{o}C for 30 minutes after which the excess Iodine was removed by adding a saturated solution of sodium thiosulfate until the dark color of Iodine is visibly removed. The ether layer was separated and washed with water and collected. The resulting ether solution was dried over sodium sulfate, concentrated and distilled (95^{o}C at 0.5 mmHg) to give **3** in 85% yield.

(E)-1-chlorotetradec-4-ene (5)

To a flame dried flask under argon was added non-1-ene (0.48 mmol, 60.2 mg) and dry THF (0.3 mL). 9-borabicyclo[3.3.1] nonane (9-BBN) (0.5 M in THF, 0.477 mmol, 0.95 mL) was slowly added to this mixture at 0^{o}C and slowly warmed up to room temperature. After stirring for 6 hours, (E)-5-chloro-1-iodopent-1-ene (0.43 mmol, 100 mg), [1,1'-bis(diphenylphosphino)-ferrocene]dichloropalladium (II) complex with dichloromethane (1:1) (3 mol%, 0.013, 10.6 mg), sodium hydroxide (1.3 mmol, 3M, 0.43 mL) and additional THF (1 mL) were added. The mixture was refluxed for 16 hours under vigorous stirring. The resulting dark mixture was diluted with hexanes (3 mL), washed with brine, and dried over magnesium sulfate. The crude mixture was purified over a column with hexanes to give desired product **5** in 75% yield.

N,N-dimethyl-3-(trimethoxysilyl)propan-1-amine (7)

Dimethylamine (2.0 M in methanol. 81.6 mmol, 40.8 mL) was added to neat (3-chloropropyl)trimethoxysilane (10.88 mmol, 2 mL) and refluxed at 90^{o}C for 24 hours. Excess dimethylamine and methanol were removed under vacuum to give a yellow solid which was washed with pet ether and filtered. The filtrate was concentrated and distilled (95^{o}C at 0.5 mmHg) to give the desired product **7** as a clear liquid in 40% yield.

(E)-N,N-dimethyl-N-(3-(trimethoxysilyl)propyl)tetradec-4-en-1-ammonium chloride (8)

Compound **7** (14.46 mmol, 3 g) was added to a solution of **5** (16 mmol, 3.67 g) stirring in methanol (6 mL) in a round bottom flask purged with argon. The mixture was heated to reflux at 90^{o}C for 3 days. The mixture was then concentrated under vacuum, washed twice with hexanes and then further dried under vacuum to give **8** in 51% yield.

Electrochemical Impedance Spectroscopy

Electrochemical impedance was measured in the frequency range from 1 Hz to 1 MHz at an a.c. measuring voltage of 100 mV with a potentiostat/galvanostat and frequency response analyzer (Solatron 1287/1260). The setup used for the proton conductivity measurements is shown in Figure S1. The measurements were performed by sandwiching the sample in the sample holder (made of Torlon plastic) between two Pt/Ir (80:20) electrodes. Measurements were made initially under 100% R.H. at room temperature and then also at variable temperature. The temperature range between 25^{o}C and 95^{o}C was explored by using a digital temperature controller (Watlow) hooked up to Kapton heaters sandwiched between brass coolers and the main brass block as shown in Figure S-1. The temperature was measured with an accuracy greater than +/- 0.1^{o}C. The membrane conductivity was calculated using Eq. (1)

$$\sigma = l / RS \qquad (1)$$

where σ is the ionic conductivity, l the distance between the two electrodes (i.e. the thickness of the pellet) measured with a digital micrometer at a constant torque of 46 inch-ounce, R is the resistance of the membrane and S the cross-sectional area of the pellet i.e. the electrode area.

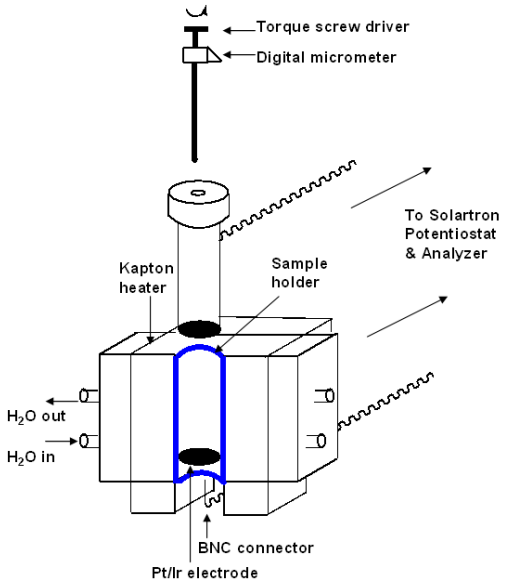


Figure S-1

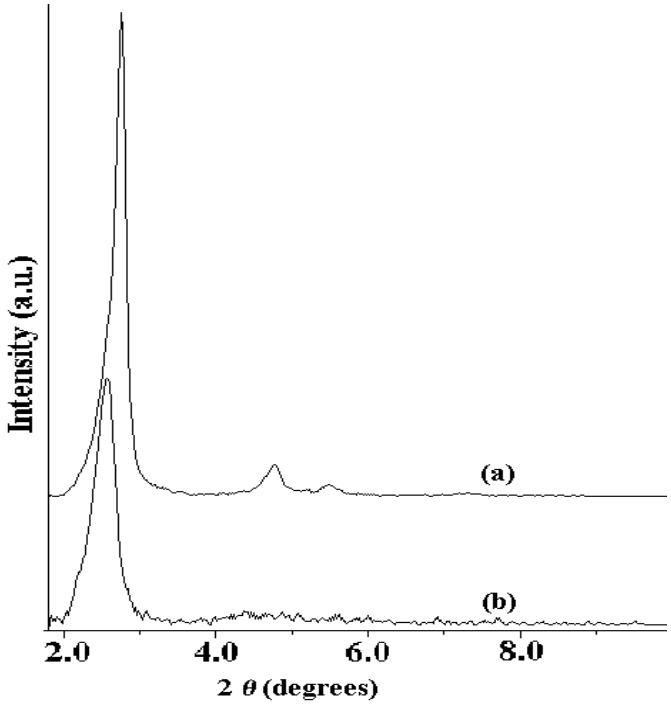


Figure S-2: XRD patterns of MCM-41 before (a) and after ozonolysis (b)

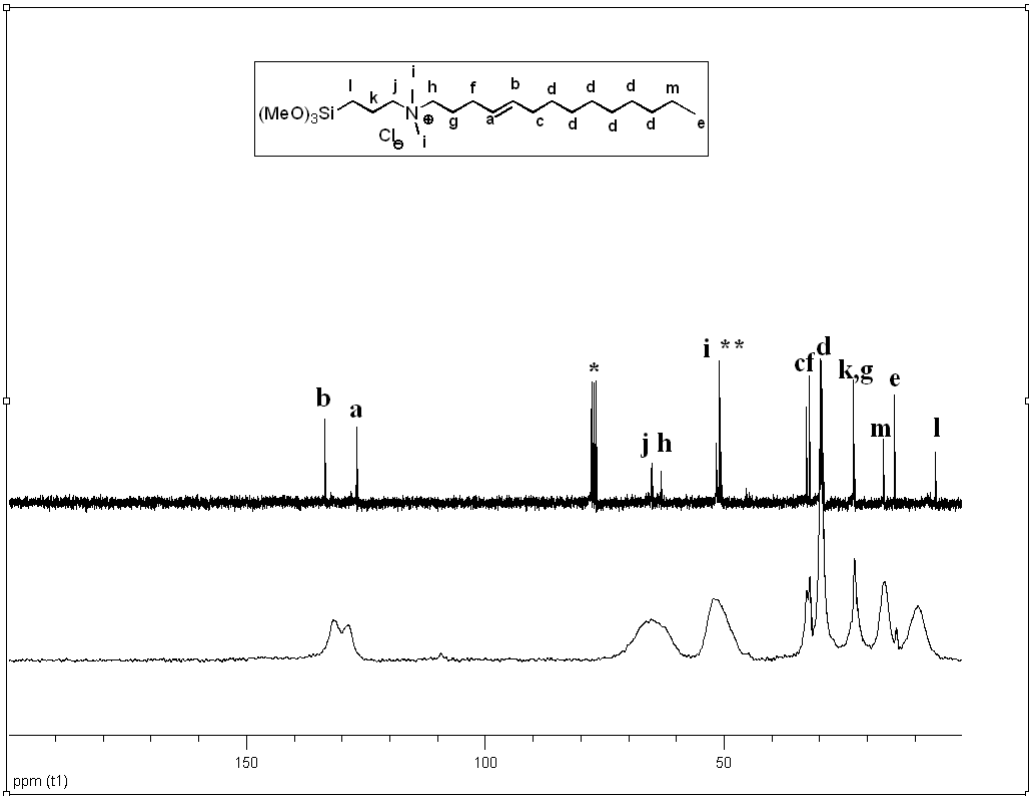


Figure S-3: ^{13}C MAS NMR of liquid phase in $CDCl_3$ and solid phase of **8**

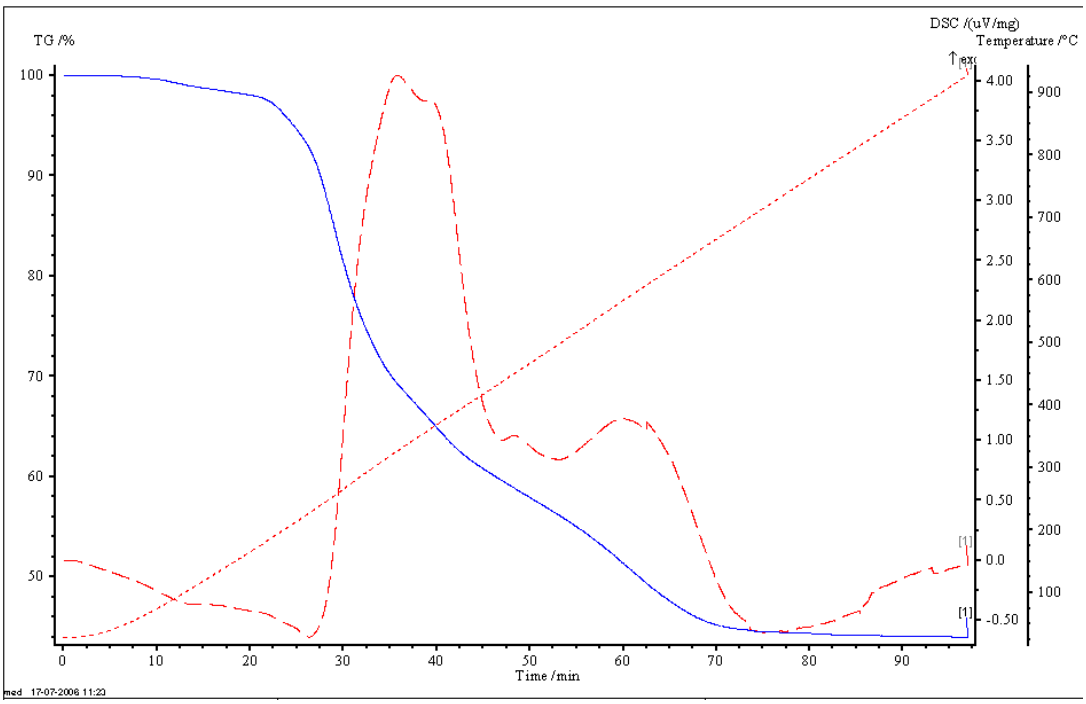


Figure S-4: TGA of MCM-41-C(4)-acid. Loading assuming full condensation = 2.53 mmol/g. Loading assuming one uncondensed methoxy group = 2.21 mmol/g.

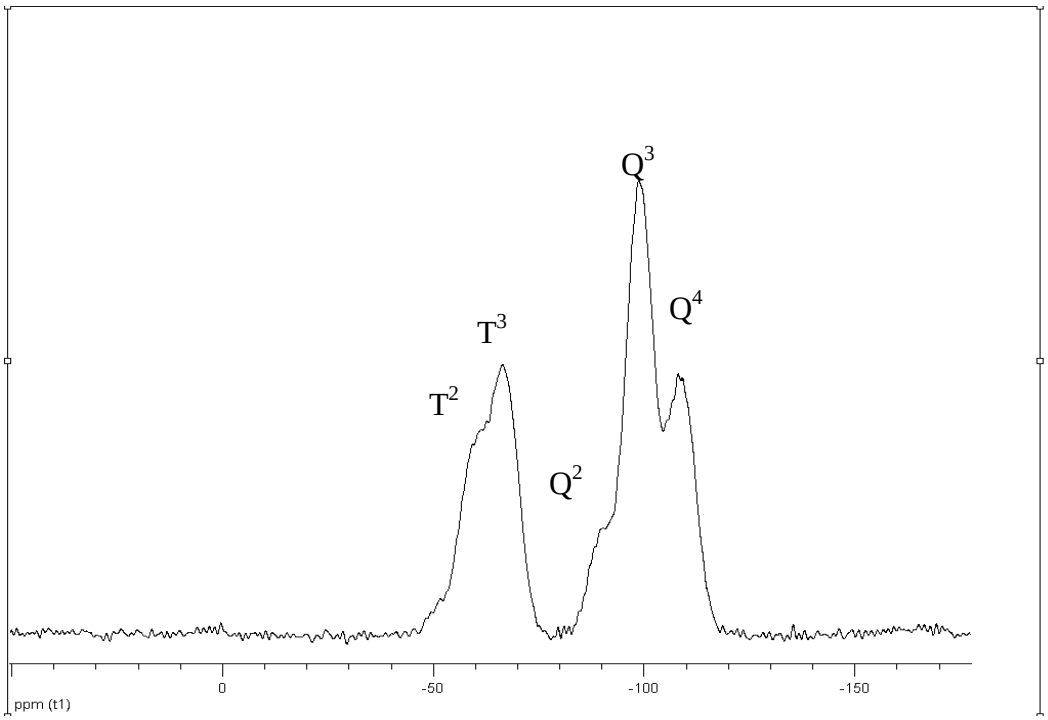


Figure S-5: ^{29}Si CP NMR of MCM-41-C(4)-acid.

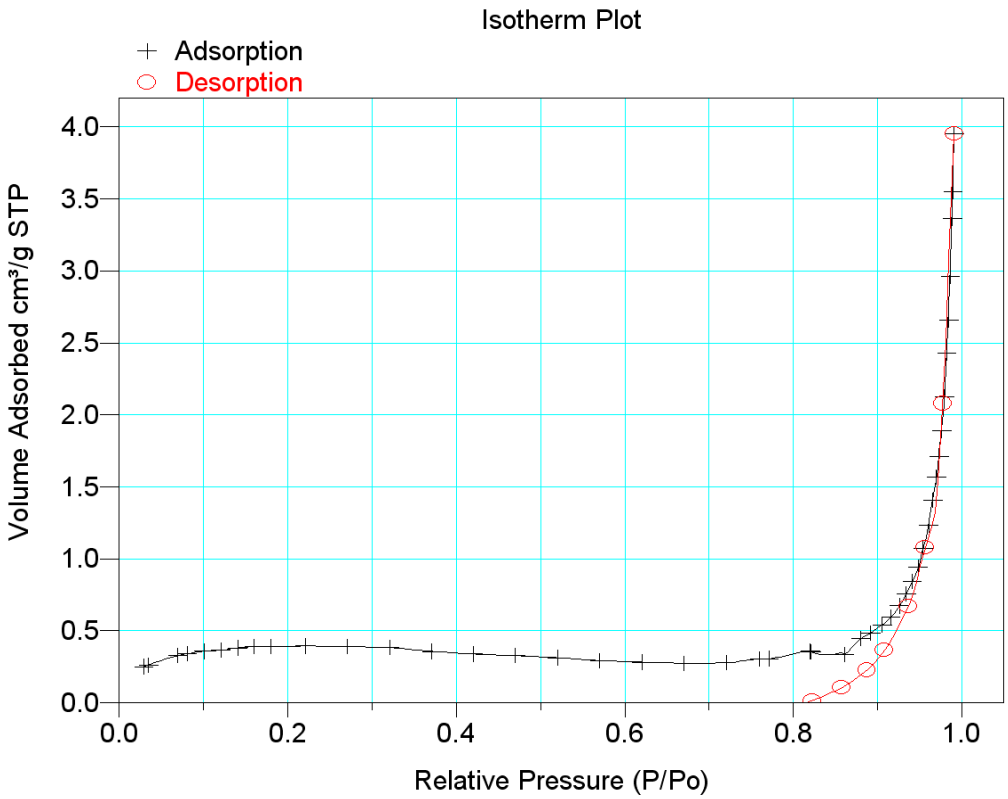


Figure S-6: N_2 Adsorption/Desorption Isotherm of MCM-41-C(4)-acid.

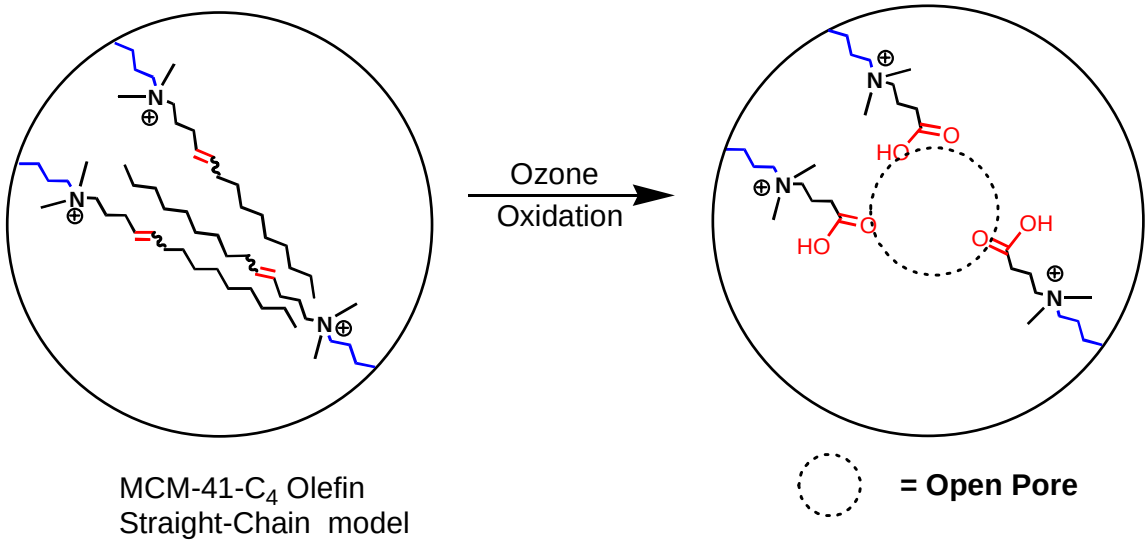
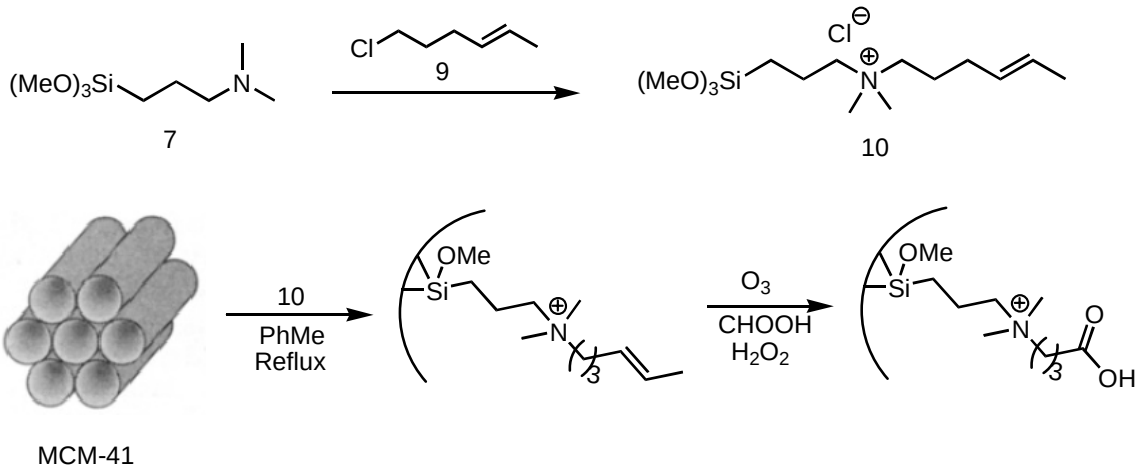


Figure S-7: Schematic diagram illustrating straight chain mechanism



Scheme S-1: Preparation of grafted material

(E)-N,N-dimethyl-N-(3-(trimethoxysilyl)propyl)hex-4-en-1-ammonium chloride (10)

Compound **7** (38.4 mmol, 7.97 g) was added to a solution of **9** (40 mmol, 4.78 g) stirring in methanol (8 mL) in a round bottom flask purged with argon. The mixture was heated to reflux at 95^{o}C for 3 days. The mixture was then concentrated under vacuum, washed twice with hexanes and then further dried under vacuum to give **10** in 60% yield.

Grafting and Ozonolysis procedure for the C(4)-acid grafted material

Compound **10** (1.84 mmol, 0.6 g) was dissolved in toluene (90 mL) and added to calcined mesoporous MCM-41. The mixture was heated to reflux for 24 hours under vigorous stirring. After cooling down to room temperature, the mixture was filtered, washed with acetone and extracted using a soxhlet apparatus in dichloromethane overnight. The resulting powder was then dried overnight.

Ozonolysis was carried out by bubbling ozone (84 µg/mL) through a suspension of the grafted MCM-41 (1 g) material in dichloromethane (60 mL) at -78^{0}C. After 7 hours, the solution was purged with argon while warming to room temperature, filtered and washed with acetone and water. Oxidation of the ozone treated solid was carried out with formic acid (5 mL) and hydrogen peroxide (2.5 mL) in water (2.5 mL) at 50^{o}C for 1 hour followed by a 1N hydrochloric acid (10 mL) post treatment for another hour to give the corresponding carboxylic acid groups. The solids were then washed with acidic ethanol at 50^{o}C to remove any adsorbed species.